§20. Micellar Shape Transition in Amphiphilic Solutions: A Molecular Dynamics Study

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Amphiphilic molecules such as lipids and surfactants consist of both a hydrophilic part and a hydrophobic part. In aqueous solutions, these molecules spontaneously self-assemble into various structures such as micelles, bilayer membranes and bicontinuous structures[1]. The micellar shape transition plays an important role in cellular physiology and drug delivery systems[2]. Although numerous computer simulation studies have been performed on micellar systems in amphiphilic solutions to date[3], the detailed mechanisms of the micellar shape transition in amphiphilic solutions have not been fully understood at the molecular level. The purpose of this study is to clarify the molecular mechanisms of the micellar shape transition in amphiphilic solutions. With a view to investigating the effect of the hydrophilicity on the micellar shapes in amphiphilic solutions at the molecular level, we carry out the molecular dynamics (MD) simulations of coarse-grained rigid amphiphilic molecules with explicit solvent molecules and systematically analyze the micellar shape transitions[4].

The computational model is the same as that used in the previous work[5]. An amphiphilic molecule is a rigid rod that consists of one hydrophilic particle and two hydrophobic particles. A solvent molecule is modeled as a hydrophilic particle. The interaction between a hydrophilic particle and a hydrophobic particle is modeled by the repulsive soft core potential and all other interactions are modeled by the Lennard-Jones potential. Here, the interaction parameter $\varepsilon^*_{\rm hs}$ between a hydrophilic head particle and a solvent molecule represents the intensity of the hydrophilic interaction. The equations of motion for all particles are solved numerically by using the leap-frog algorithm at constant temperature with a time step of $\Delta t^* = 0.0025$ and the temperature is controlled at every 10 time steps by *ad hoc* velocity scaling. We apply the periodic boundary conditions and the number density is set at $\rho^* = 0.75$. Initially, we prepare an isolated micelle of 97 amphiphilic molecules with $\varepsilon^*_{\rm hs}$=1.0 in solution at $T^* = 1.3$. The number of solvent particles is 5541, which leads to the amphiphilic concentration of 0.05. The intensity of the hydrophilic interaction $\varepsilon^*_{\rm hs}$ is then varied ($\varepsilon^*_{\rm hs}$=0.1, 0.2, ..., 0.9, 1.1, 1.2, ..., 5.0) and MD simulations of $t^* = 2.0 \times 10^4$ (8.0×10^6 time steps) are carried out for each simulation run.

In Fig. 1, the fraction of various micellar shapes and the slope of the total potential energy are shown as a function of the intensity of the hydrophilic interaction $\varepsilon^*_{\rm hs}$. Figure 1(a) shows that the dominant micellar shape is disc for $\varepsilon^*_{\rm hs} < 1.6$, cylinder for $1.6 < \varepsilon^*_{\rm hs} \leq 2.2$ and sphere for $\varepsilon^*_{\rm hs} \geq 3.3$. There exists a wide coexistence region in the intensity of the hydrophilic interaction between the cylinder and the sphere for $2.3 \leq \varepsilon^*_{\rm hs} \leq 3.2$ although There exists a narrow coexistence region between the cylinder and the disc, which is located around $\varepsilon^*_{\rm hs} \approx 1.6$. It is also found from Fig. 1(b) that, as $\varepsilon^*_{\rm hs}$ increases, the slope of the total potential energy decreases stepwise in relation to the micellar shape transition although the total potential energy itself decreases monotonically even during the micellar shape transition.

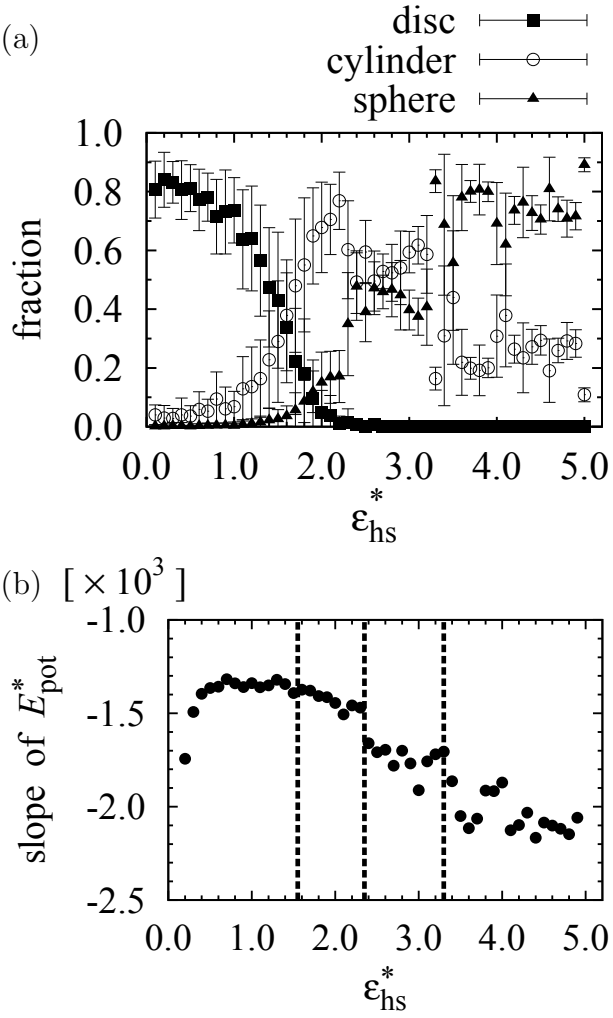

Fig. 1. (a) The fraction of various micellar shapes and (b) the slope of the total potential energy versus the hydrophilic interaction parameter $\varepsilon^*_{\rm hs}$.

1) Hamley, I.W., *Introduction to Soft Matter* (J. Wiley, Chichester, 2007) Rev. ed.
2) Chaudhuri, A., Haldar, S. and Chattopadhyay, A.: Chem. Phys. Lipids **165** (2012) 497.
3) Brodskaya, E. N.: Colloid J. **74** (2012) 154.
4) Fujiwara, S., Hashimoto, M., Itoh, T., Nakamura, H. and Tamura, Y.: J. Phys.: Conf. Ser. (in press).
5) Fujiwara, S., Itoh, T., Hashimoto, M. and Horiuchi, R.: J. Chem. Phys. **130** (2009) 144901.